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ORIGINAL ARTICLE

Assessment of fluoride contaminations in groundwater of hard rock aquifers in Madurai district, Tamil Nadu (India)

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Abstract The fluoride contamination in drinking water is already gone to the alarming level and it needs the immediate involvement and attention of all people to solve this problem. Fluoride problem is higher in hard rock terrains in worldwide and Madurai is such type of hard rock region. Totally 54 samples were collected from the Madurai district of Tamilnadu with respect to lithology. The samples collected were analysed for major cations and anions using standard procedures. The higher concentration of fluoride is noted in the Charnockite rock types of northern part of the study area. 20 % of samples are below 0.5 ppm and 6 % of samples are above 1.5 ppm exceeding the permissible limit. The affinity between the pH and fluoride ions in groundwater suggests that dissolution of fluoride bearing minerals in groundwater. The higher concentration of fluoride ions are observed in the lower EC concentration. The isotopic study suggests that fluoride is geogenic in nature. In factor scores, fluoride is noted in association with pH which indicates the dissolution process.

Keywords Groundwater · Fluoride · Lithology · Weathering

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Introduction

The highly reactive fluorine exists in the form of fluoride in natural waters (Leung and Hrudey 1985). Fluoride is a naturally occurring element in groundwater which originates mainly from the natural sources and causes significant health impacts. The recommended value of fluoride in drinking water prescribed by the WHO (2008) standard is 1.5 mg/l. Fluorosis is said to be a worldwide problem. It has been reported that nearly 20 developing countries (Mameri et al. 1998) and 17 states in India (Yadav and Khan 2010) are affected by fluorosis including Tamilnadu. It is estimated that 200 million peoples in the world of 20 countries are affected by this endemic disease and in Indian continent 62 million peoples are affected from fluorosis from the drinking of fluoride rich water. 150,000 villages in India are affected by the dental fluorosis problem. It plays a vital role in the formation of dental enamel and normal mineralization of bones when it is present in less quantity (Chouhan and Flora 2010). Fluoride health problems are common in semi-arid regions in many countries (Jacks et al. 2005; Reddy et al. 2010). The fluoride concentration less than 0.5 mg/l leads to the risk of tooth decay (Abu-Zeid 1998) and the concentration above

1.5 mg/l causes the endemic disease called dental fluorosis (Handa 1975; Ripa 1993).The primary adverse effects associated with chronic, excess fluoride intake are dental and skeletal fluorosis (Susheela 1993). Fluoride in groundwater is mainly controlled by local and regional geology, lithology and their flow directions and also they are aided by semi-arid climate of the region (Umarani and ramu 2014; Saxena and Saxena 2014). Fluoride content in groundwater is mainly due to natural contamination, but the process of dissolution is still not well understood (Ripa 1993; Saxena and Ahmed 2001).The higher fluoride in the groundwater of hard rock regions have been carried out by various researchers (Chidambaram et al. 2013; Manivannan et al. 2012; Singaraja et al. 2012; Manikandan et al. 2012).Weathering of minerals and formation of Calcium and Magnesium carbonates serves the good sinks for the fluoride in groundwater (Srinivasamoorthy et al. 2008). In Bakreswar and Birbhum regions of west Bengal fluoride contamination arise by industrial pollution from the manufacture of steel, aluminium and fertilizers, whereas fluorapatite is used as a source of phosphorous (Datta et al. 2014). The usage of phosphatic fertilizer into the soil in agricultural activities also causes potential fluoride in groundwater (Loganathan et al. 2006).

The fluoride concentration in groundwater of the surrounding districts of Madurai like Dindugal (Manivannan 2010), Tiruchirapalli (Ramesh et al. 2012), Sivaganga (CGWB 2010) have also been the earlier studies shows that certain location of Madurai district is also reported to have high fluoride (CGWB 2008) >1.5 ppm. It is also understood that there is continuation of lithology from the surrounding district and moreover hard rock terrains are commonly reported to have high concentration of fluoride in groundwater (Chidambaram 2000). The increase of temperature and the quantity of water consumed are also the main causes of fluorosis in the other part of the study area (Manivannan et al. 2012; Chidambaram et al., 2013). The higher concentration of fluoride in India has been resulted due to the dissolution of fluorite, apatite, micas, amphiboles with OH, F group and they are mostly observed in the Igneous and Metamorphic rocks (Chidambaram 2000; Manikandan et al. 2012). Many people suffer from the fluorosis in the world due to the intake of fluoride rich groundwater (Zhang et al. 2003) and in the study area the groundwater is the main sources of drinking water. Keeping these factors in mind an attempt has been made to identify the sources of fluoride, its distribution in groundwater with respect to lithology to categorise the fluoride affected areas spatially and to delineate the interrelationship of fluoride with other major ions in groundwater.

Study area

General details

The study area lies in the north latitude of 9°33′3.6″ and 10°19′8.4″ and east longitude of 77°27′7.2″ and 78°28′58.8″ covering an 3741 km^2 in southern part of Tamilnadu (Fig. 1). There are seven taluks in this district namely Madurai-North, Madurai-South, Melur, Vadipatti, Usilampatti, Peraiyur and Thirumangalam. The major river system that feeds the Madurai is Vaigai river basin which separates the district into two parts. The average rainfall of this district is 902 per annum. The topography of the area ranges between 160 and 1400 m above mean sea level (Sankar 2002). More than 85 % of the soil in this district is classified as red soil. The study area experiences a semi-arid climate (CGWB 2008). Madurai is one of the few rubber growing areas in South India and there are rubber-based industries.

Lithology

The lithology comprises fissile hornblende biotite gneiss, charnockite, granites, quartzites and floodplain alluvium along the river (GSI 1995). Madurai district falls in the southern granulite terrains. Massive Charnockite of

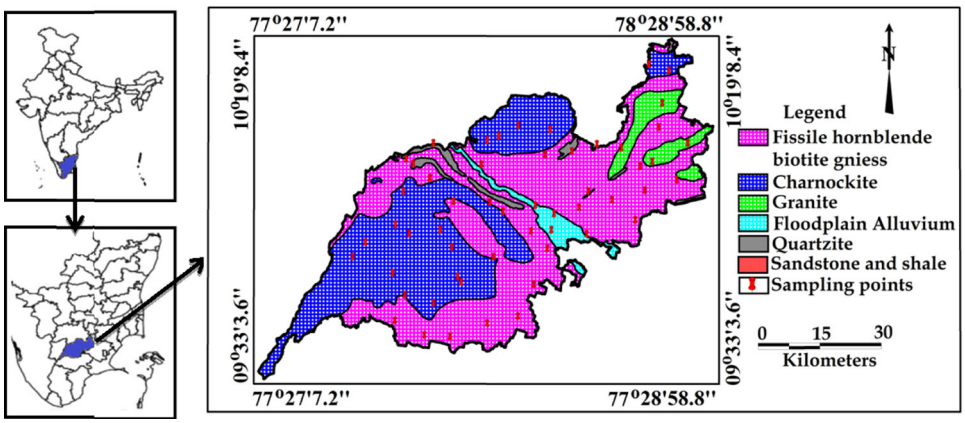

Fig. 1 Study area map with lithology and sampling points

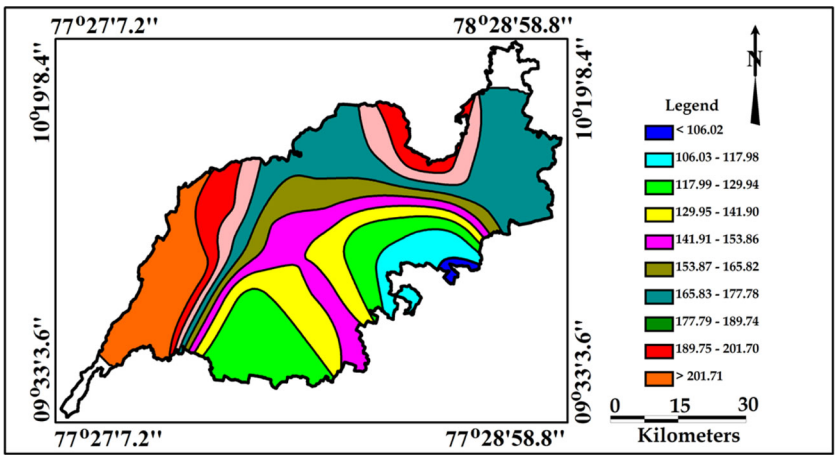

Fig. 2 Water level map of the study area (in meters above mean sea level)

comparatively high mafic appearance are observed in this terrain (Srikantappa et al. 1985). Mafic Charnockite (two pyroxene granulite) having major mineral assemblage of clinopyroxene, orthopyroxene, hornblende and plagioclase. The khondalite shows a general mineralogy of K feldspars, quartz, garnet, biotite, sillimanite, cordierite, spinel and plagioclase, with graphite, apatite and zircon as major accessories (Baiju 2006).

Water level

The entire district is mainly covered by the hard rock regions and the groundwater occurs in the weathered part of the hard rocks, fractures, fissures and joints (CGWB 2007). The aquifers range from Archaean to Recent alluvium. The ground water level in this district varies according to the formation of rocks. The reduced water level with respect to sea level is shown in figure (Fig. 2). The figure shows that the greater levels of depth to water table were noted in the southern and the northern/north-eastern part of the study area. It also indirectly indicates that the ground water moves towards the eastern part of the study area. The deepest groundwater level is noted along the Vaigai river.

Methodology

Sample collection and preparation

A total of 54 groundwater samples were collected from the handpumps representing the entire study area in premonsoon season. Sampling and analysis were carried out using standard procedures (Ramesh and Anbu 1996; APHA 1995). Groundwater samples were collected in a 500 ml polyethylene bottles after pumping out the stagnant water for 20 min in handpump, in order to get representative samples. Then, it was sealed and brought to the laboratory for analysis, stored properly (4 °C) and filtered with 0.45 μm filter paper before analysis. The pH and TDS were determined in the field using the field kit (Eutech handheld instruments).

Fluoride ion analysis

Fluoride (F^-) concentration was determined using Orion fluoride ion electrode model (94-09, 96-09). The instrument was checked for slope by TISAB III (concentrate with CDTA) using the metre with millivolt read only mode (APHA, 1995; Manikandan et al. 2012). The electrode is rinsed with distilled water, blot dry and placed into the beaker. When the stable reading is displayed, the mv values for the corresponding standard concentration (0.05, 0.1, 1, 1.5, 2.5, 5, 10, and 100 ppm) were noted. 50 ml of more concentrated standard and 5 ml of TISAB III was taken, stirred thoroughly and the readings were measured. The electrode was rinsed with deionized water, blot dry and place into the second beaker—where stable reading was displayed, then mv value was recorded and corresponding standard concentration was plotted in semi logarithmic graph paper. Later calibration curve was prepared by plotting the mv values on the linear axis, and the standard concentration values on the logarithmic axis. 50 ml of sample was taken with 5 ml of TISAB III, stirred thoroughly. The electrode is rinsed into the deionized water blot dry and placed into the beaker. When a stable reading is displayed, the mv value was again measured. Using the calibration curve prepared the unknown concentration is determined using Orion fluoride ion electrode.

Major and minor ion analysis

The calcium, magnesium, bicarbonate and chloride were determined by titrimetric method. The sodium and

potassium were analysed through flame photometry (CL 378). The dissolved silica, phosphate and sulphate were determined by spectrophotometry (Hach 6000).

Isotope analysis

Groundwater samples were collected separately in a 60 ml capacity clean polyethylene bottle. The sample bottles were filled completely and preserved air tight in order to avoid evaporation. The experiments were carried out and the results are within ±10 % error. The stable isotopes $\delta^{18}O$ and δD were measured by mass spectrometer (Finnigan deltaplus Xp, Thermo Electron Corporation, Bermen, Germany) using gas equilibration method with a precision of 0.5 and 0.1 ‰ (2σ criterion), respectively. Stable isotope results were expressed with respect to VSMOW (Vienna Standard Mean Ocean water) in units δ (‰) where

$$\delta = (R_{\text{sample}} - R_{\text{SMOW}}/R_{\text{SMOW}}) \times 10^3,$$

where $R = D/H$ or $^{18}O/^{16}O$

Data analysis

In this study, statistical analyses such as correlation coefficient, factor analysis and factor scores were used for understanding the dataset attained in the study area using Statistical Package of Social Studies (SPSS) version 17. Correlation matrix was extracted by the principal component analytical (PCA) method. Factor extraction was completed with a minimum acceptable Eigen value of 1. The varimax rotation method was used to extract the rotated factor. The PCA method was used to obtain and extract the correlation matrix (Olobaniyi and Owoyemi 2006). Totally four factors were extracted for four seasons and they were categorised according to factor loadings. Factor score coefficients are derived from the factor loadings. Factor scores were computed for each sample by a matrix multiplication of the factor score coefficient with the standardised data. The value of each factor score represents the importance of a given factor at the sample site. The spatial distribution of the factors score have been plotted using Map INFO professional 8.5 software.

Results and discussion

The maximum, minimum and average values of the major ions are given in Fig. 3, fluoride ion concentration (Fig. 4) of the present and surrounding districts given in Table 1 and the stable isotope values in groundwater is given in Table 2.

pH ranges from neutral to alkaline in nature. Ca ranges from 20 to 276 mg/l and Mg ranges from 1.20 to 98.40 mg/l may be due to the weathering process of rock water interaction in groundwater (Srinivasamoorthy et al. 2008). Na ranges from 18 to 278 mg/l and K ranges from 0.10 to 147.20 mg/l. Na and K are mainly derived from the weathering of feldspars present in the Charnockite and the

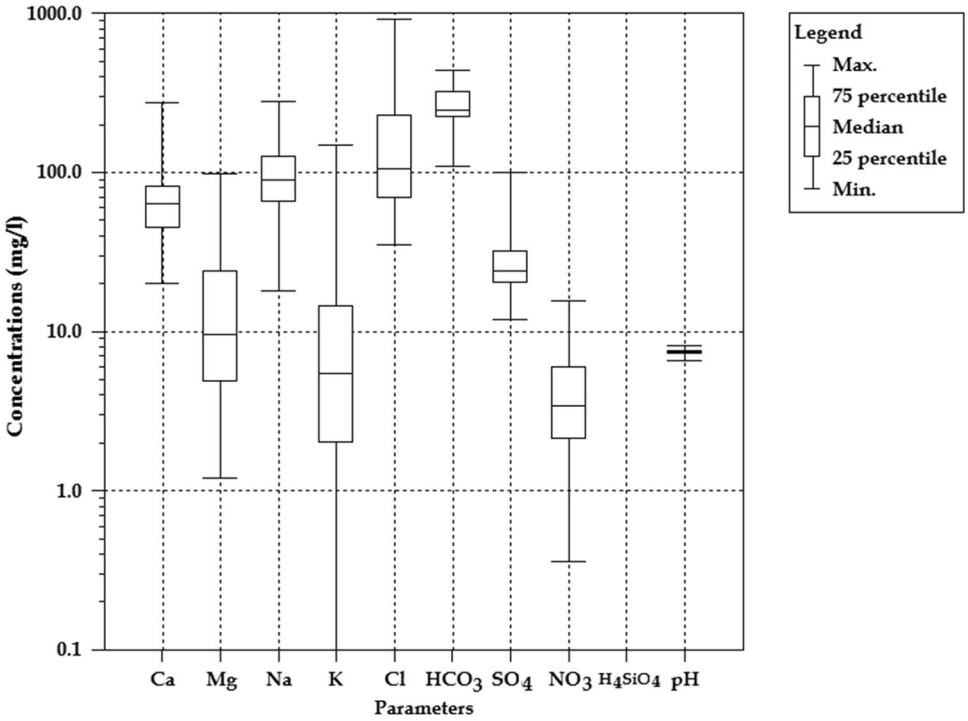

Fig. 3 Box and Whisker plot for groundwater samples

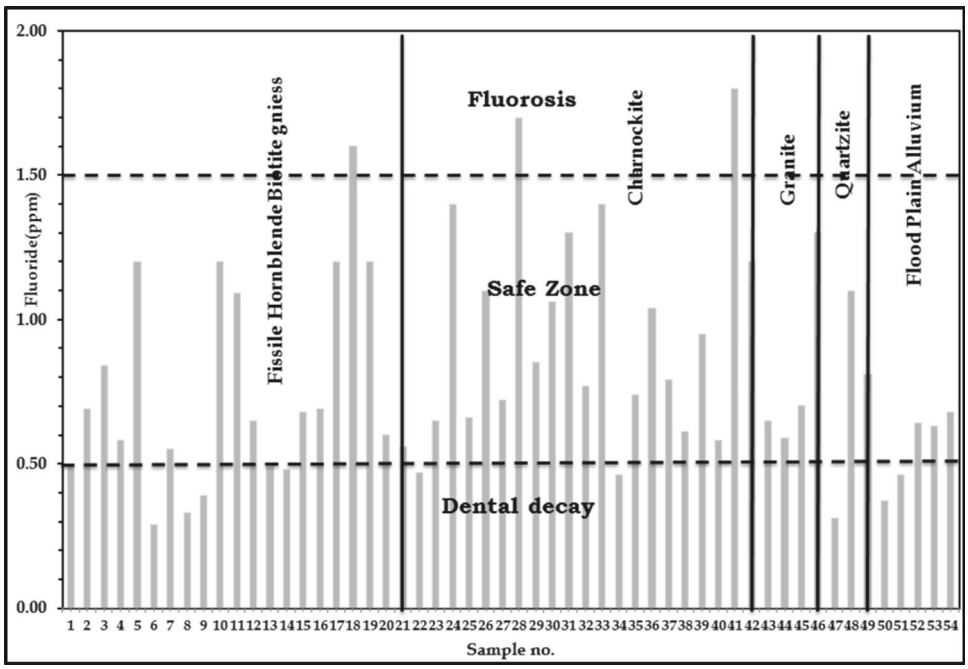

Fig. 4 Fluoride concentration in groundwater samples with respect to lithology

Table 1 Fluoride concentration in surrounding districts

S. No	Fluoride concentration (mg/l)		Area	Reference
	Minimum	Maximum		
1	0	3	Erode	Chidambaram (2000)
2	0.37	4	Salem	Srinivasamoorthy et al. (2008)
3	0.5	5.45	Krishnagiri	Manikandan (2014)
4	0.1	2.5	Dindugal	Manivannan (2010)
5	0	3.3	Tuticorin	Singaraja et al. (2012)
6	0.29	1.8	Present study Madurai	

Table 2 The maximum, minimum and average values of fluoride in ppm and stable isotope in ‰

	Fissile hornblende biotite gneiss ($n = 21$)	Charnockite ($n = 21$)	Granite ($n = 4$)	Quartzite ($n = 3$)	Flood plain alluvium ($n = 5$)
Fluoride					
Maximum	1.6	1.8	1.3	1.1	0.68
Minimum	0.29	0.46	0.59	0.31	0.37
Average	0.75	0.96	0.81	0.74	0.56
δD (‰)					
Maximum	−13.00	−25.65	−29.86	−22.98	−10.99
Minimum	−45.10	−37.61	−33.40	−29.98	−31.89
Average	−28.79	−32.06	−32.17	−26.72	−21.55
$\delta^{18}O$ (‰)					
Maximum	−1.37	−3.61	−4.61	−3.30	−0.98
Minimum	−6.44	−5.50	−5.00	−4.33	−4.80
Average	−4.11	−4.69	−4.83	−3.83	−3.16

fissile hornblende biotite gneiss formations (Thivya et al. 2013a). Cl ranges from 35 to 925 mg/l observed along the Vaigai river course may be due to the sewage disposal (Ranjana and Champa Naverathna 2011). HCO_3 ranges from 109.80 to 439 mg/l are mainly due to the weathering process (Stumm and Morgan 1996). NO_3 ranges from 0.36 to 15.50 mg/l, PO_4 ranges to 3.50 mg/l and SO_4 ranges from 12 to 100 mg/l may be due to fertilizer in agricultural activities. H_4SiO_4 ranges from 2.50 to 72.00 mg/l may be due to weathering of silicate minerals. EC ranges from 441 to 2900.00 µS/cm whereas the higher value is noted along the course of the Vaigai river may be due to sewage infiltration (Thivya et al. 2013a). Ca, Mg, Na, K, Cl, HCO_3, pH exceeds 37, 17, 2, 19, 33, 19 and 2 % in groundwater samples, respectively. NO_3 and SO_4 are within the permissible limit (WHO 2004). The order of dominance of major ions are $Na > Ca > K > Mg = Cl > HCO_3 > SO_4 > H_4SiO_4 > NO_3 > PO_4$. The order of dominance of fluoride in various lithologies is as follows

Charnockite > Fissile hornblende biotite gneiss > Granite > Quartzite > Floodplain alluvium

Spatial distribution of fluoride in groundwater

The samples analysed for F^- were spatially marked in the bubble plot with size proportionate to the ion. The higher concentration of fluoride ions are noted in the northern part of the study area which is represented by the Charnockite rocks (Fig. 5) and the same lithology extends to the Dindugal district where the higher concentration of fluoride was observed (Manivannan 2010).

In the study area the pH ranges from 6.6 to 8.2. Most of the samples are alkaline in nature, hence it favours the solubility of fluoride bearing ions in groundwater (Manivannan et al. 2012). The higher concentration of fluoride is noted in the pH range of 7.5 to 7.8, and there is an increasing trend is noted (Fig. 6). The hydroxides with the higher pH concentration replace the fluoride containing minerals like muscovite, and thus it increases the concentration of fluoride in groundwater (Gupta et al. 2012).The dissolution of fluoride in groundwater depends on the pH concentration. At higher pH hydrolysis takes place where $(OH)^-$ is released into the system with more cations and fluoride.

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- = Al_2[AlSi_3O_{10}][OH^-]_2 + 2F^- + K^+$$

The higher concentration of fluoride is noted in the samples with lower EC (Fig. 7). This may be due to the release of F from fresh weathered rocks during the process of weathering. HCO_3 is noted to be higher in charnockite samples indicates the process of weathering or dissolution (Srinivasamoorthy et al. 2008; Prasanna et al. 2008). The higher concentration of fluoride is noted in the samples with lesser HCO_3 in charnockite which indirectly indicates lesser intensity of weathering with the dissolution process (Fig. 8) or may be due to hydrolysis (Manikandan 2014).

Isotopic approach

Environmental isotopes δD and $\delta^{18}O$ data gives an idea about the secondary processes in the groundwater. The plot of $\delta\ ^{18}O$ and δD of the rainwater samples of the Tamilnadu (Chidambaram et al. 2007) was drawn to derive the local meteoric water line (LMWL). Some samples of flood plain alluvium, granite and quartzite show enriched values resembling evaporation trend (Fig. 9). The samples of fissile hornblende biotite gneiss and charnockite are recharged by precipitation and most of the FHBG samples are recharged by evaporating water bodies which is represented by the enriched isotopes and they fall away from LMWL. It is also evident that study area has more tanks and in addition to agricultural activities (Thivya et al. 2013b), which contributes significant moisture to the

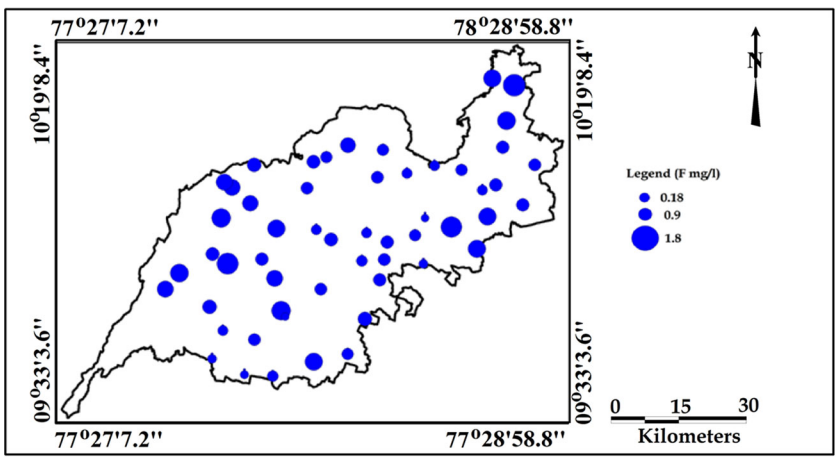

Fig. 5 Spatial distribution of fluoride ions in groundwater samples

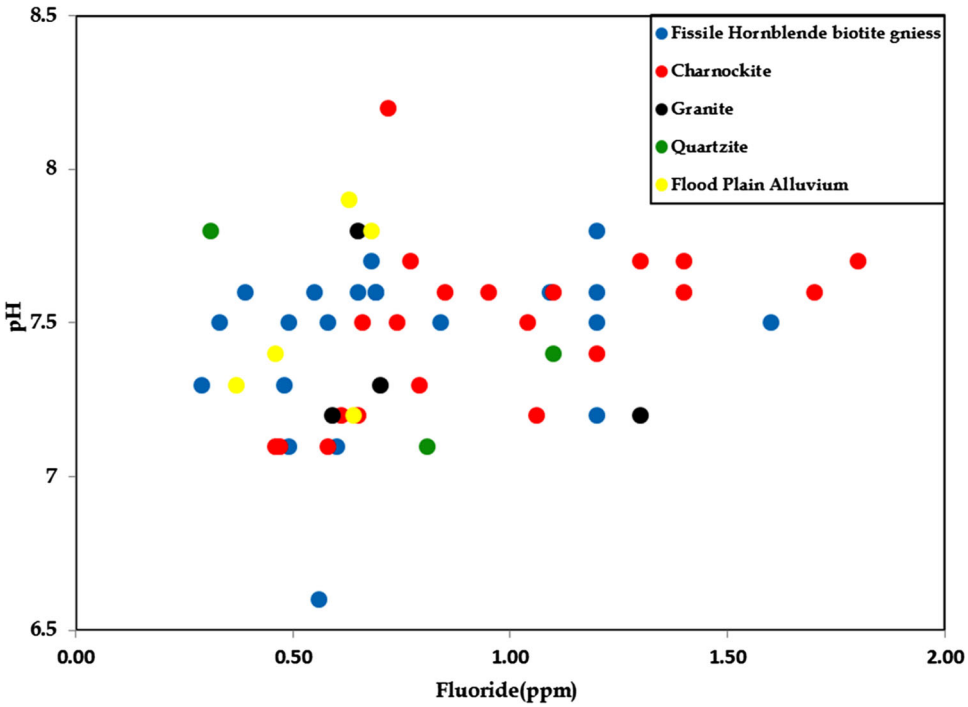

Fig. 6 Fluoride vs. pH diagram for groundwater samples

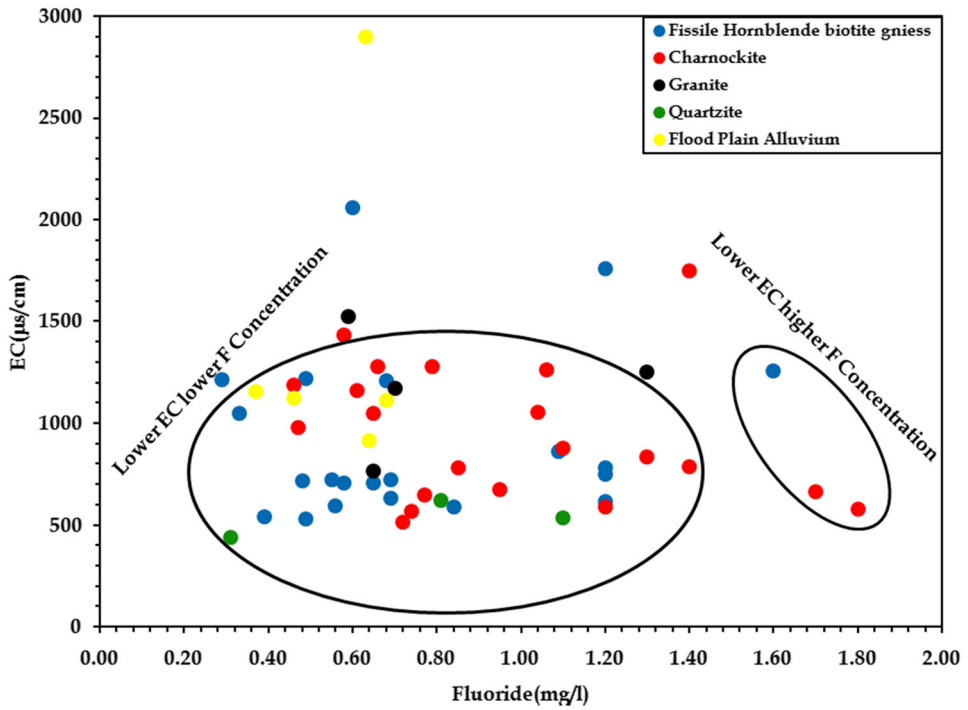

Fig. 7 Fluoride vs. EC diagram for groundwater samples

atmosphere. There is a clear representation that most of the water samples lie close to the LMWL. Rock-water interaction may also enrich $\delta^{18}O$ (Prasanna et al. 2008).

The higher concentrations of fluoride are noted in depleted isotopic composition whereas the lower concentration is noted in enriched isotopic composition (Fig. 10a). Low fluoride may be due to variations in the degree of weathering of fluoride source minerals in different types of rocks (Tirumalesh et al. 2007). The samples of flood plain alluvium and fissile hornblende biotite gneiss are enriched in nature which may be due to recharge by evaporated water bodies such as tanks and surface waters river Vaigai.

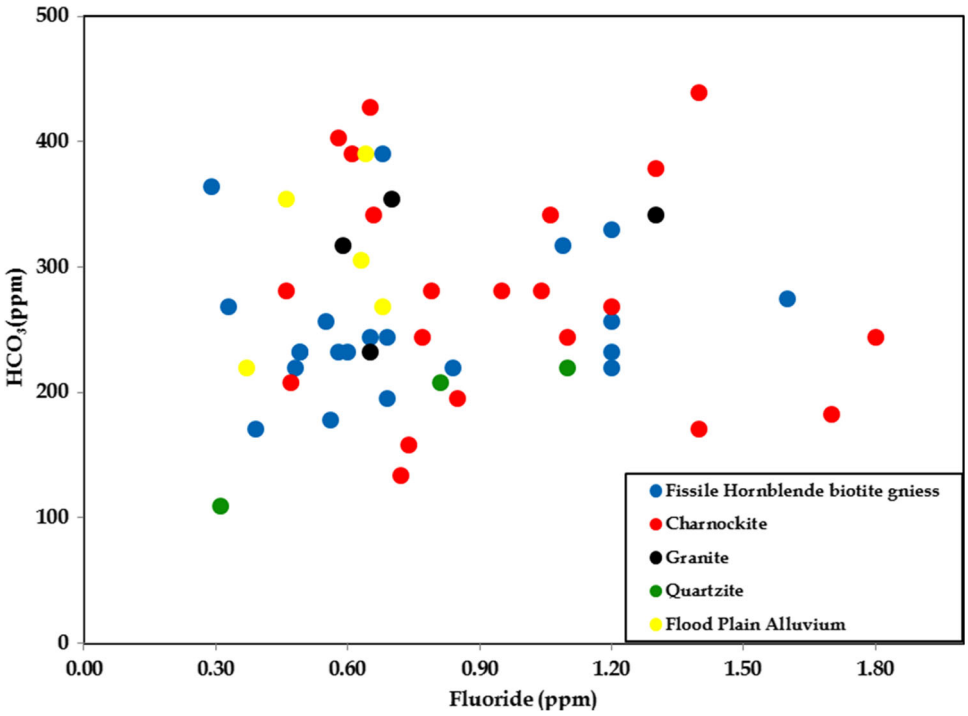

Fig. 8 Fluoride vs. HCO_3 diagram for groundwater samples

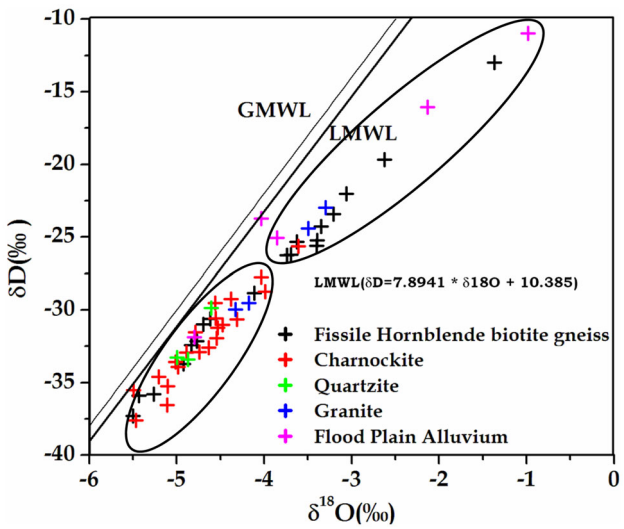

Fig. 9 Plot for $\delta^{18}O$ versus δD of groundwater samples compared with GMWL and LMWL

But the EC of the floodplain water is more, which may be due to the infiltration of the domestic sewage, urban waste along floodplain alluvium. The charnockite, granite and quartzite samples are depleted it may be due representation of recharge due to rainfall. The dissolution of apatite/hydroxyapatite in charnockite releases the F^- in groundwater (Manikandan 2014). In fissile hornblende biotite gneiss the F^- may be released due to the ion exchange processes and residence time enhances the higher concentration in groundwater (Subbarao 2003). The Apatite/Fluorapatite in Charnockite are also major contributors of F^- (Ramanathan 1956; Chidambaram 2000). High fluoride concentrations in groundwater are likely to be result of the dissolution of Biotite, which may contain significant fluorine at the OH^- sites of their octahedral sheet (Chidambaram et al. 2007; Liu et al. 2003). The FHBG groundwater sample with higher F^- concentration shows enriched isotope values. This is mainly due to the rock-water interaction (Prasanna et al. 2008), which also enhances the ion exchange process. In charnockite the samples with higher F^- show depleted isotope values indicating a different process. Hence, this is mainly due to the dissolution process. The F^- present in apatite in dissolved in the groundwater during the normal process of weathering (Chidambaram 2000). Apatite percentage in charnockite varies from 0.27 to 0.7 in charnockites (Subbarao 2003). Hence, it is inferred that F^- contributed by the FHBG is due to the ion exchange process and that of charnockite is due to apatite dissolution. This process absorbs the hydrogen ion, and thus it lowers the pH concentration in groundwater.

Generally d-excess values ranges between 8 and 10, it is assumed the samples may be evolved from primary precipitation. The d-excess value in the precipitation can be greater than if the evaporation in the source region takes place under lower humidity (Gat 1981). Samples show d-excess values ranging from −4 to 10 ‰ which could be attributed to primary precipitation. The increasing trend is

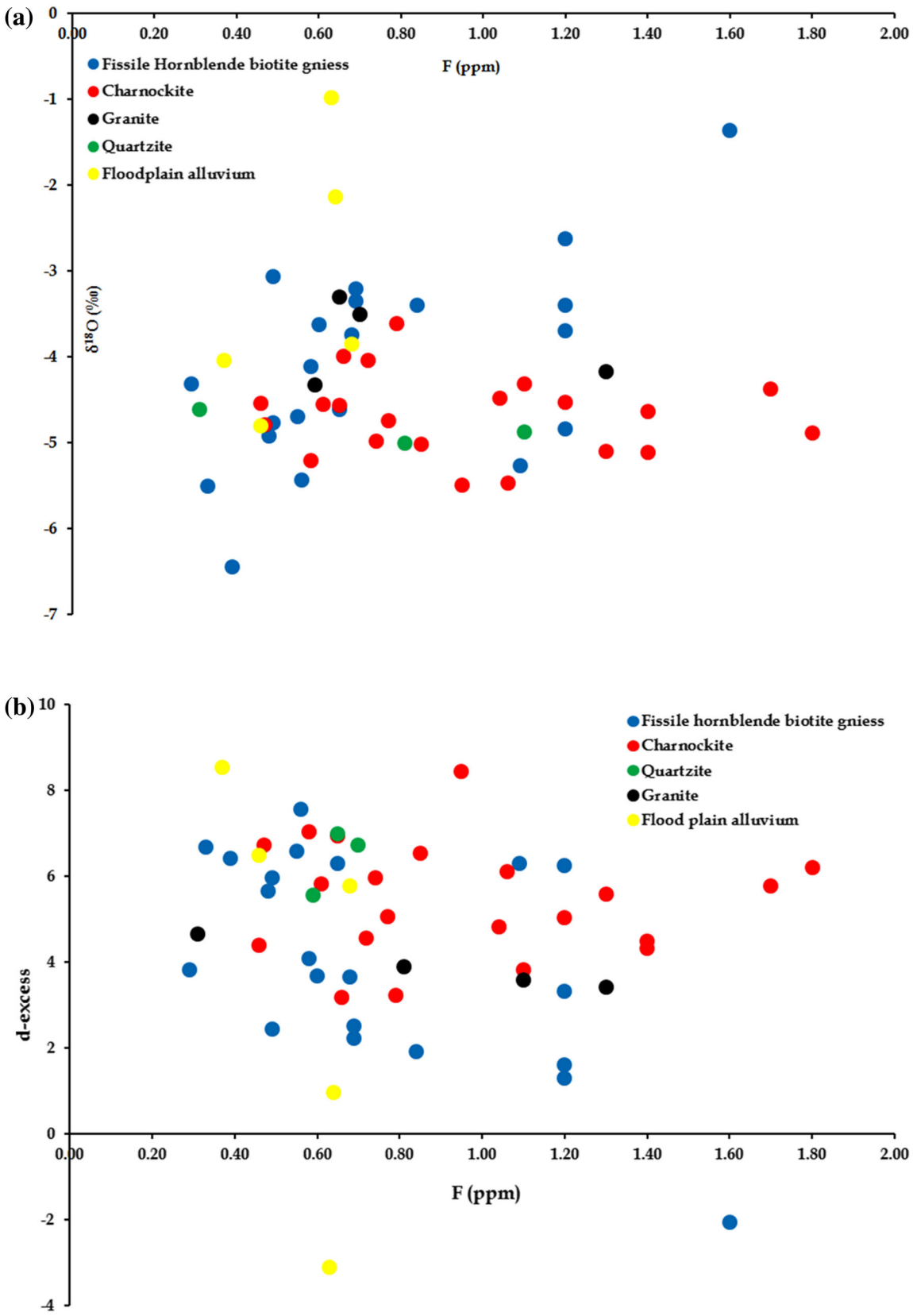

Fig. 10 **a** Bivariate plot between $\delta^{18}O$ and F in groundwater. **b** Bivariate plot between d-excess and F in groundwater

noticed in charnockite samples with d-excess, decreasing trend is noticed in granitic samples whereas no trend is observed with other lithological types (Fig. 10b). The concentration of F^- in groundwater with d-excess values <3 ‰ may be due to evaporative enrichment (Harvey 2005). The higher concentration of fluoride is noted in between 4 and 6 ‰ which may be due to the enrichment of fluoride ions by primary precipitation.

Correlation analysis

The correlation between the fluoride and other ions suggests that poor positive correlation with Na, HCO_3, NO_3, H_4SiO_4 and pH (Table 3). The poor negative correlation exists between fluoride with Ca, Mg, K and SO_4. The poor positive correlation between the fluoride and pH suggest that fluoride enrichment due to the dissolution of fluoride in the aquifers (Yidana et al. 2012). The poor positive correlation between the HCO_3 and F^- suggests the weathering of minerals contributes the fluoride ions in groundwater.

Factor analysis

The PCA analysis with varimax rotation is used to identify the causative factors to delineate the fluoride chemistry and distribution in the groundwater. Liu et al. (2003) classified the factor loadings as 'Weak', 'Moderate' and 'Strong' corresponding to absolute loading values of 0.3–0.5, 0.5–0.75 and >0.75, respectively. In the study area Factor 1 is represented by Cl, Ca, Mg, Na, NO_3 and SO_4 which indicates the anthropogenic activities predominate with the weathering process in the study area (Table 4). The Factor 2 is represented by K and HCO_3 suggest the weathering process.

Table 4 Rotated component matrix of groundwater samples

	Component			
	1	2	3	4
Ca	0.80	−0.46	−0.14	0.06
Mg	0.77	−0.40	−0.27	−0.02
Na	0.61	0.41	0.44	0.19
K	0.37	0.68	−0.31	−0.22
Cl	0.92	−0.22	0.08	0.18
HCO_3	0.47	0.63	0.11	−0.12
NO_3	0.77	0.14	0.21	−0.07
F	−0.12	0.09	0.68	0.11
PO_4	−0.14	0.20	−0.03	0.78
SO_4	0.76	−0.01	0.08	0.15
H_4SiO_4	0.20	−0.35	0.34	−0.53
pH	−0.24	−0.18	0.73	−0.06
Temp	0.07	0.47	−0.07	−0.31

The loadings of factor 3 are F^- and pH which indicates the dissolution of fluoride minerals. Fissile hornblende biotite gneiss and charnockite are the major sources for the fluoride ions in the groundwater (Chidambaram 2000), whereas in the charnockite the apatite and fluorapatite minerals are the major contributors of fluoride ions. Hence, the higher concentration of fluoride is noted in Charnockite rocks of the study area.

$$(Na)_2(Ca,\ Mg,\ Fe)_3Al_2Si_6O_{20}(OH,\ F)_4 + H_2O \leftrightarrows (Mg_3Fe_3)\ Al_3Si_5O_{20}(OH) + OH + F + Na + Mg + HCO_3$$

The spatial distribution of higher concentration is noted only in the northern part of the study area. Thus it is evident that the enrichment of fluoride ions in groundwater

Table 3 Correlation analysis of fluoride with other parameters in groundwater

	Ca	Mg	Na	K	Cl	HCO_3	NO_3	F^-	PO_4	SO_4	H_4SiO_4	pH
Ca	1.0											
Mg	0.8	1.0										
Na	0.2	0.1	1.0									
K	0.0	0.1	0.2	1.0								
Cl	0.9	0.7	0.6	0.1	1.0							
HCO_3	0.1	0.2	0.5	0.5	0.2	1.0						
NO_3	0.5	0.5	0.5	0.3	0.6	0.5	1.0					
F	−0.2	−0.2	0.1	−0.2	−0.1	0.1	0.1	1.0				
PO_4	−0.1	−0.1	0.1	0.0	0.0	0.0	−0.1	0.0	1.0			
SO_4	0.5	0.5	0.5	0.3	0.7	0.2	0.5	−0.1	−0.1	1.0		
H_4SiO_4	0.2	0.2	0.1	0.0	0.2	0.0	0.1	0.1	−0.2	0.0	1.0	
pH	−0.2	−0.3	0.0	−0.3	−0.1	−0.2	−0.1	0.2	0.0	0.0	0.2	1.0

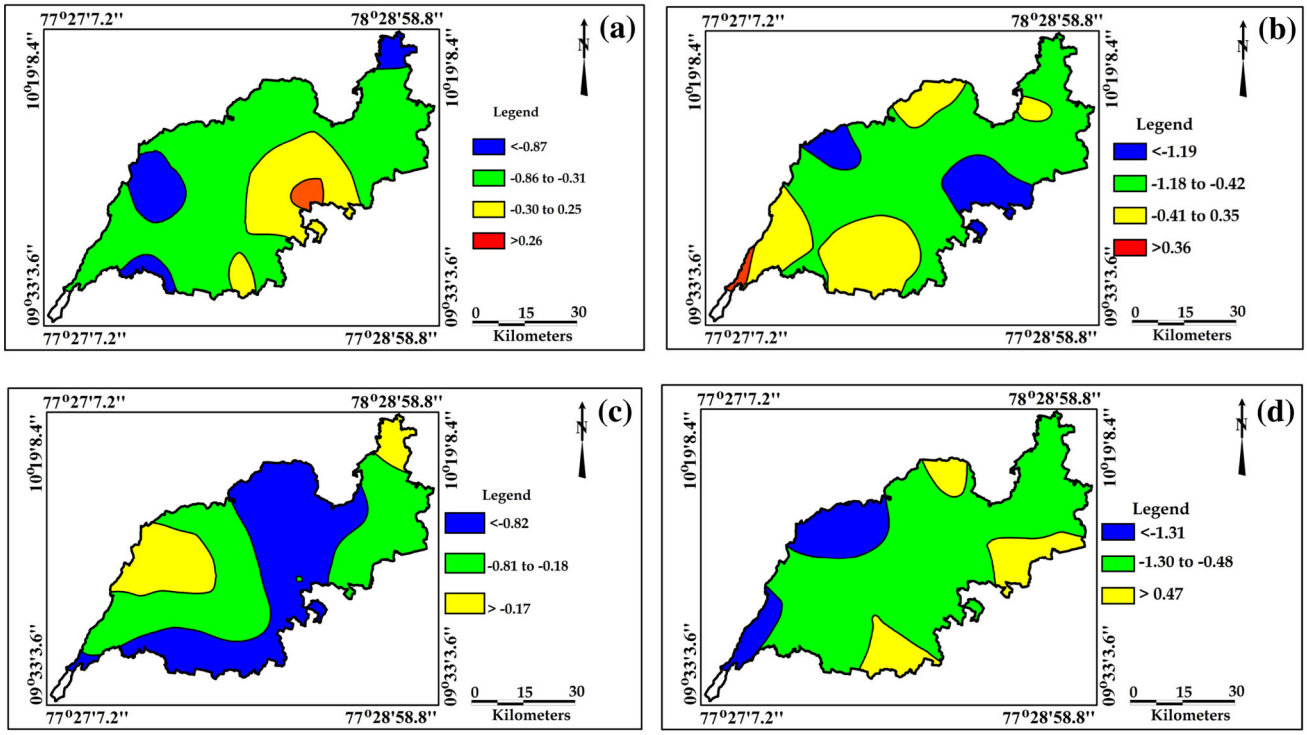

Fig. 11 **a–d** Spatial distribution of factor scores 1, 2, 3, 4, respectively

depends on the concentration of pH. Factor 4 is represented with the PO_4 resembles the agricultural impact in the study area. The higher Na may be exchanged for the hydroxides in the weathered matrix in the host rocks may increase the pH (Manivannan 2010).

The factor score was used to find out the spatial variation of the factor and to identify the zone of its representation. The positive zones indicate the dominance of that factor, hydrogeochemical regime (Chidambaram et al. 2007). The higher concentration of factor 1 is noted in the north eastern part of the study area where the Vaigai river discharges. This may be due to the sewage infiltration (Thivya et al. 2013a) (Fig. 11a). The factor 2 is highly observed in the southern part of the study area where the weathering process is dominant (Fig. 11b). In factor 3 the higher concentration is observed in the northern (charnockite) and south western part (FHBG region) of the study area. The higher concentration of fluoride is also noted in the northern part of the study area (Fig. 11c). The factor 4 is highly observed in the southern part of the study area with patches where the agricultural process is dominant (Fig. 11d). It is interesting to note that spatial distribution of fluoride concentration in the study area matches with the hydrogeochemical active regions derived from the factor scores in the northern part of the study area indicates that fluoride in groundwater is found at the source (Manikandan et al. 2012) and the higher concentration is also observed in the south western part of the study area indicates that pH dissolution is also dominant in that regions.

Conclusion

The above study indicates that geogenic factors are responsible for high levels of fluoride in groundwater in the study area. The higher concentration of fluoride is observed in the Charnockite rocks which lies in the northern part of the region suggest that there is the lithological control in the distribution of fluorides. The pH plays a vital role in the dissolution and leaching of fluoride into the groundwater. The dissolved silica lacks representations in the factor loadings resembles that fluoride is less influenced by the silicate weathering. The highest fluoride concentration is observed in the lower EC indicates the fresh weathering of rocks that liberates the F^- ions in groundwater. It is inferred from the stable isotopic relations that F^- released from FHBG is due to ion exchange and that of charnockite is due to dissolution of apatite. The observations made in the study area indicate the spatial variability of fluoride in groundwater, and there is a need for the sustainable planning and management of groundwater to safe and secure life of the people in the region.

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